

# Plasma Graft Polymerization of Vinylimidazole onto Kapton Film Surface for Improvement of Adhesion Between Kapton Film and Copper

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## SYNOPSIS

Kapton film was modified by means of the plasma graft polymerization of vinylimidazole for the improvement of the adhesion with copper metal. Argon plasma exposure generated hydroperoxides at the surface of the Kapton film. Hydroperoxides generated by the argon plasma exposure could initiate the graft polymerization of vinylimidazole. The graft polymerization was restricted at the surface of the Kapton film and never occurred on the inside of the Kapton film. The graft polymer layer was 150–200 nm thick. The surface modification by the plasma graft polymerization of vinylimidazole led to the improvement of adhesion between Kapton film and copper metal. A part of the copper metal made a complex with imino groups in the vinylimidazole chains graft-polymerized onto Kapton film. The complex is considered to contribute to the improvement of the adhesion. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Polyimide is a super performance polymer with high-temperature resistance, good mechanical properties, flame resistance, dimensional stability, and a low dielectric constant. Kapton® H is commercially provided as a polyimide film from E. I. Du Pont de Nemours & Co., and is widely used as an insulating and pattern-delineating material in the field of microelectronics industry. Usually, Kapton film used for these applications is supplied as one metallized with copper metal by means of the vacuum evaporation technique, the sputtering technique, the ion plating technique, etc. In the metallization, poor adhesion between Kapton film and copper metal is a subject to be settled for good application.

To improve the adhesion between Kapton film and copper metal, many investigators have studied the surface modification of Kapton film from a theoretical and practical viewpoint.<sup>1–12</sup> Chou and Tang<sup>1</sup> investigated the interaction occurring at the interface between Kapton film and metal in the me-

tallization process. Their conclusion was that a metal–oxygen–carbon complex was formed at the Kapton film–metal interface. The complex contributed to strong adhesion. It was difficult to make a complex with copper metal and Kapton film, but it was easy to make the complex with chromium metal. Thus, they proposed a new metallization process, a combination of chromium and copper metals: first, a trace of chromium metal was deposited at the surface of the Kapton film to make the complex, and then the copper metal was deposited on the chromium layer. This conclusion suggests the importance of a special functionality capable of making a strong interaction with copper metal.

Xue et al.<sup>13</sup> reported that benzimidazole interacted with copper metal at zero oxidation state to make a complex. The complex, when a copper sheet was coated with polymers, acted as a promoter of adhesion to make strong adhesion between copper sheet and the polymers.

We are interested in the complex between benzimidazole and copper metal, and expect that if imidazole groups were introduced onto the Kapton film surface, the imidazole groups could act as a functionality to make a complex, and a strong adhesion between Kapton film and copper metal would be ac-

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completed. With this in mind, we investigated the plasma graft polymerization of vinylimidazole onto the Kapton film surface in order to introduce imidazole groups onto the Kapton film surface and discussed effects of the graft polymerization on the adhesion.

## EXPERIMENTAL

### Material

Polyimide film used in this study was poly[(*N,N'*-oxydiphenylene) pyromellitimide], Kapton® H, that was kindly provided from Toray Du Pont Co. and was 508 mm wide and 25  $\mu\text{m}$  thick. The film was washed with acetone using an ultrasonic washer prior to the plasma graft polymerization experiments. 1-Vinylimidazole, which was purchased from Tokyo Kasei Kogyo Co., was used as a monomer for the graft polymerization. Vinylimidazole was distilled under vacuum just before the graft polymerization experiments. Low-density polyethylene sheet (density 0.92  $\text{g}/\text{cm}^3$ , 250  $\mu\text{m}$  thick, Idemitsu Petrochemical Co.) also was used for the comparison with the Kapton film in the effect of the argon plasma exposure. The polyethylene sheet does not contain additives without antioxidant. The polyethylene sheet was washed with acetone using an ultrasonic washer prior to the argon plasma exposure experiments.

### Plasma Graft Polymerization

The plasma graft polymerization of vinylimidazole at the Kapton film surface was carried out in two steps: the formation of hydroperoxides at the Kapton surface and the graft polymerization initiated by the hydroperoxides. In the formation of hydroperoxides, the Kapton surface was exposed to an argon plasma, and subsequently exposed to air to generate hydroperoxides which were able to initiate the graft polymerization. In the graft polymerization step, the Kapton film having hydroperoxides was immersed in a benzene solution of vinylimidazole (5 vol %), and the polymerization reactions were continued under nitrogen atmosphere in the temperature range of 40–80°C for 24 h. Each of the steps is described fully.

### Formation of Hydroperoxide

The formation of hydroperoxides at the Kapton surface was carried out in two steps: the radical formation by argon plasma exposure and peroxidation of the radicals by air exposure. For the argon plasma

exposure, a home-made reactor that was a capacitively coupled system at a 13.56-MHz frequency (Samco International Inc., Japan, model FRG-200). The reactor consisted of a glass tube (170 mm diameter, 300 mm long), a gas inlet with a micrometering valve (Whitey Co., U.S.A., model SS-22RS4), a pressure gauge (Datametrics Co, U.S.A., capacitance manometer type, model 622), and a vacuum system (Daia Vacuum Engineering Co. Ltd., model DSSO-422) consisting of a combination of a diffusion (150 L/s) and a rotary pump (200 L/min). There was a substrate stage on the inside of the glass tube and electrodes for glow discharge on the outside of the glass tube. A schematic diagram of the reaction system is shown in Figure 1.

The Kapton films (50  $\times$  10 mm) were mounted on the substrate stage. The reaction chamber was evacuated to approximately 0.13 Pa, and then argon gas was introduced into the reaction chamber at a pressure of 13.3 Pa. Afterward, the films were exposed to argon plasma (at an RF input power of 5–100 W) for 5–60 s. Immediately after the plasma exposure, the films were taken from the reaction chamber and exposed to air for 5–10 min at room temperature in order to be peroxidized.

### Graft Polymerization

The peroxidized Kapton films were immersed in a benzene solution of vinylimidazole (5 vol %), and the graft polymerization was initiated and continued under nitrogen atmosphere at 40–80°C for 24 h. Prior to the graft polymerization, vinylimidazole used as a monomer was distilled, and the benzene solution was degassed by repeat freezing and melting procedures to eliminate oxygen dissolved in the solution. The graft-polymerized films were washed with methanol for 12 h using a Soxhlet apparatus to eliminate homopolymers of vinylimidazole, and dried at 50°C under vacuum. The percentage of grafting polymers ( $G$  in wt %) was estimated from Eq. (1):

$$G = \frac{W_1 - W_0}{W_0} \quad (1)$$

where  $W_1$  and  $W_0$  are the weight of the graft-polymerized film and the original, respectively.

### Hydroperoxide Concentration Generated at Kapton Film Surface

The concentration of hydroperoxides generated at the Kapton film surface by the argon plasma and the air exposure was determined by means of the

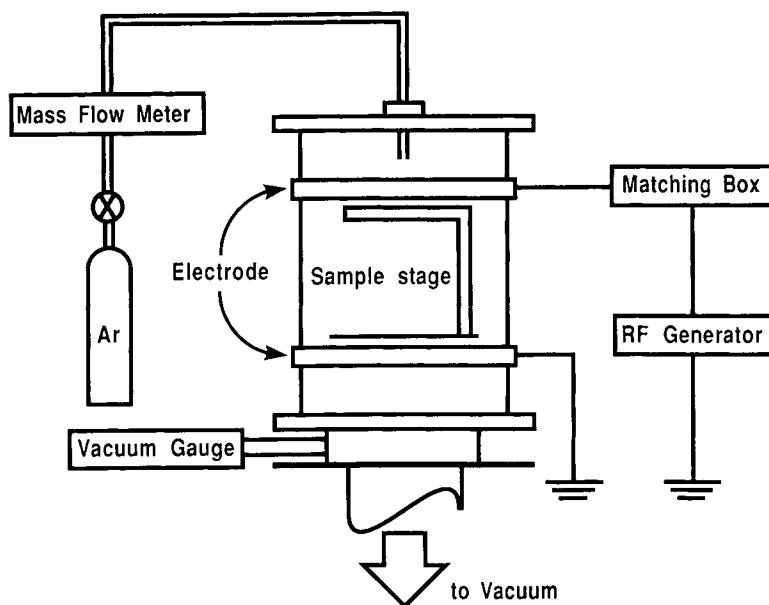


Figure 1 Schematic diagram of plasma reactor.

iodide method.<sup>14</sup> The Kapton film exposed to the argon plasma and air was reacted with sodium iodide in a isopropanol–benzene solution (6 : 1 vol. ratio) containing a trace of ferric chloride (1 ppm) at 60°C for 10 min. Oxidation reactions of iodide ions by hydroperoxides in the Kapton film led to the formation of  $I_3^-$  ions of which the maximum absorption appeared at 360 nm. From the absorption intensity at 360 nm, the concentration of hydroperoxide was determined.

### Infrared (IR) Spectra

IR spectra of the plasma-graft-polymerized Kapton films were recorded in the attenuated total reflection (ATR) mode on a Horiba Fourier transform spectrometer FT300 with an MCT detector. A crystal of germanium was used as a prism for the ATR technique, and the incident angle of infrared light against the prism was 45°. The sampling depth in the range of 2000–400  $cm^{-1}$  is estimated to be about 0.66–3.3  $\mu m$ . The spectral resolution was 1.0  $cm^{-1}$  and 500 scans were recorded on each sample.

### Transmission Electron Microscope Picture of Cross Section of Plasma-Graft-Polymerized Kapton Films

The plasma-graft-polymerized Kapton films were immersed in an aqueous solution of copper nitrate (0.05M/L) whose pH value was adjusted at 4.7 with an acetic acid–sodium acetate (1 : 1) buffer solution

at room temperature for 15 h, and the imidazole groups in the graft polymers made a complex with Cu ions. Afterward, the surface of the films was rinsed with the buffer solution and then with water and dried under vacuum at 60°C for 3 h. The Cu-dyed Kapton film was sliced using a microtome, and the transmission electron microscope picture was observed with an Hitachi model HS-7D. The magnification of transmission electron microscopy was 3456 and 7200.

### Peel Strength of Adhesive Joints between Kapton Film and Copper Metal

On the Kapton films (the sample size of 5 mm wide and 50 mm long), copper metal of 200 nm thickness (99.9% purity, purchased from Nilaco Co., Japan) was deposited by the vacuum evaporation technique operated at a pressure of  $1.3 \times 10^{-3}$  Pa. Afterward, the copper-deposited Kapton films adhered to sandblasted aluminum plates using an epoxy adhesive (Japan Ablestik Co., Japan). The epoxy adhesive was cured under a pressure of 5  $kg/cm^2$  at 95°C for 70 min. Therefore, the adhesive joint is the sandwich structure of plasma-graft-polymerized Kapton film/Cu layer (200 nm thick)/epoxy adhesive/sandblasted aluminum plate. The 180° peel strength of the adhesive joints between the Kapton film and the copper metal was evaluated at a peel rate of 50 mm/min with an Instron (Instron Co, U.S.A., model 2020). The peel strength was determined from an average of ten specimens.

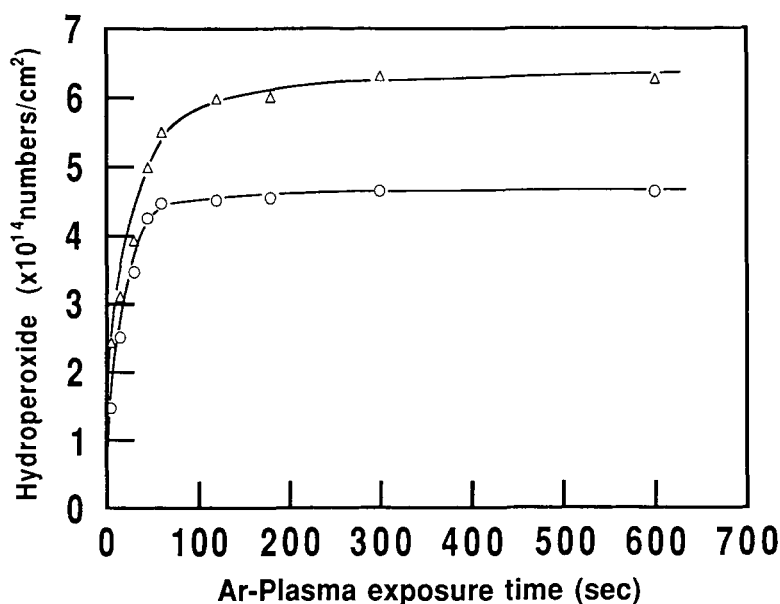
## RESULTS AND DISCUSSION

### Formation of Hydroperoxide

The combination of the argon plasma exposure and the air exposure generated some oxygen functionalities in the Kapton film. A part of these oxygen functionalities was able to oxidize iodide ions in an aqueous solution of sodium iodide into  $I_2$  (actually being  $I_3^-$  ions in the aqueous solution). This reaction was confirmed by a color change at 360 nm, and the concentration of the yielded  $I_2$  was able to be determined from the absorption intensity at 360 nm (the iodide method). Electron spin resonance (ESR) measurement showed that the Kapton film exposed to the argon plasma, but not exposed to air, contained a large number of spins, but the assignment of the spins was unsuccessful because of broad and complex ESR spectra. From two experimental evidences, there is no doubt that the argon plasma exposure generates radicals in the Kapton film and the exposure of Kapton film to the argon plasma and air generates oxidative groups such as peroxides. We can speculate that the oxidative groups may be formed from reactions of radicals generated by the argon plasma exposure with oxygen and water molecules in air. Hydroperoxide and peroxy radical may be main products which are able to oxidize iodide ions in aqueous solution of sodium iodide. In humid air, especially in the aqueous solution, the peroxy radical will react further with water molecules to

modify into hydroperoxide. Therefore, we assume that the hydroperoxide may be a main product generated by the combination of the argon plasma and air exposure. We determined the concentration of the hydroperoxide generated in the Kapton film because the hydroperoxide in Kapton film was expected to have a capability to initiate graft polymerization of vinylimidazole.

Figure 2 shows the hydroperoxide concentration generated in the Kapton film by the argon plasma operated at an RF power of 25 W as a function of the exposure time. The hydroperoxide concentration in Figure 2 is estimated in the number per unit surface area (numbers/cm<sup>2</sup>) from the assumption that all hydroperoxides were generated at the surface of the Kapton film but not at the bulk of the Kapton films. This figure indicates that the hydroperoxide concentration increases with increasing argon plasma exposure time, and levels off after an exposure time of about 60 s. The hydroperoxide concentration at the leveling-off position is  $4.5\text{--}4.6 \times 10^{14}$  numbers/cm<sup>2</sup> which is merely lower than that of the low-density polyethylene ( $6.0\text{--}6.3 \times 10^{14}$  numbers/cm<sup>2</sup>). It is surprising that the Kapton film generated hydroperoxides as much as the low-density polyethylene sheet, nevertheless the Kapton has no aliphatic carbon but does have aromatic carbon. Thus, polyethylene is composed of all aliphatic carbons. Hydrogen atoms on aromatic carbons are difficult to be abstracted by the radical and ion bombardment. The RF power dependence of the hydro-



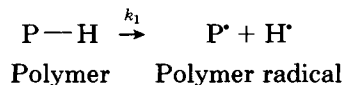
**Figure 2** Hydroperoxide concentration as a function of argon plasma exposure time (RF power, 25 W); (O) Kapton film, ( $\Delta$ ) polyethylene film.

peroxide concentration is shown in Figure 3, where the argon plasma exposure time was 60 s. The hydroperoxide concentration increases with increasing RF power, and levels off at an RF power of about 20 W. The hydroperoxide concentration at the leveled-off position is  $4.4\text{--}4.6 \times 10^{14}$  numbers/cm<sup>2</sup>. These results indicate that the argon plasma exposure at an RF power as low as 20 W and for exposure time as short as 60 s is an effective condition in formation of hydroperoxide. The argon plasma exposure at RF powers higher than 20 W and exposure time for longer than 60 s are wasteful conditions.

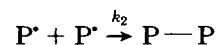
Suzuki et al.<sup>15</sup> also reported the dependence of the hydroperoxide concentration on the plasma exposure time, although they used a high-density polyethylene sheet instead of the Kapton film. When the polyethylene sheet was exposed to an argon plasma at 24 W at a 5-kHz frequency, the hydroperoxide concentration generated in the polyethylene sheet did not increase monotonously with increasing the plasma exposure time but showed a maximum at relatively short exposure time (about 5 s). They interpreted the appearance of the maximum in the hydroperoxide concentration from the competing processes between radical formation reaction by the plasma exposure and recombination reaction (disappearance) of two radicals. The interpretation is not unreasonable but means that the maximum does not always appear. Now, we consider that simple processes of the radical formation by

plasma exposure and the disappearance of radicals by recombination. Radicals remaining still in the polymer after the plasma exposure, immediately when exposed to air and water molecules, will be transformed quantitatively into hydroperoxides. Therefore, the hydroperoxide concentration generated in the polymer by the plasma exposure may be almost equal to the concentration of radicals remaining in the polymer after the plasma exposure.

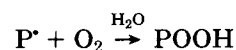
1. Radical formation by plasma exposure



2. Recombination of radicals

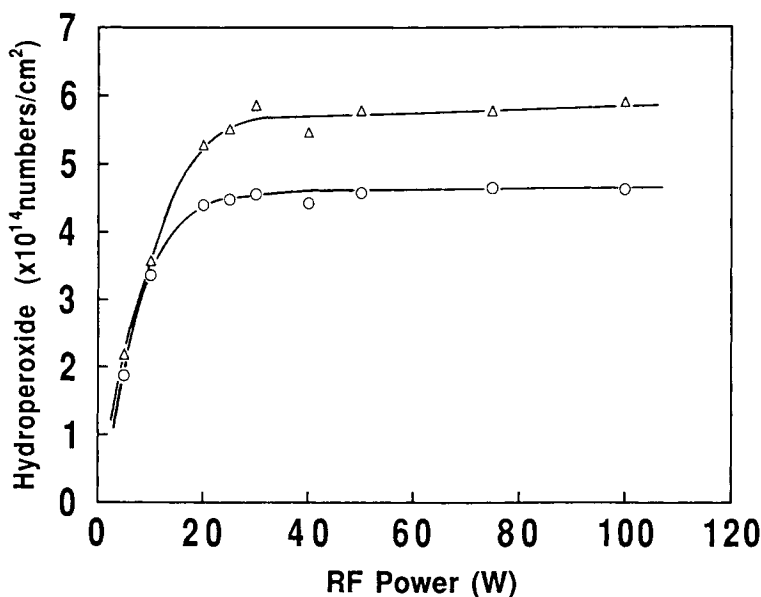


3. Hydroperoxide formation (when exposed to air)



The radical formation rate by the plasma exposure is written in Eq. (2), where  $[\text{P}^*]$  and  $[\text{P—H}]$  are the radical concentration and polymer, respectively.

$$\frac{d[\text{P}^*]}{dt} = k_1[\text{P—H}] \quad (2)$$



**Figure 3** Hydroperoxide concentration as a function of RF power (argon plasma exposure time, 60 s); (○) Kapton film, (△) polyethylene film.

The disappearance rate of radicals is written in Eq. (3).

$$\frac{d[P^*]}{dt} = -k_2[P^*]^2 \quad (3)$$

Therefore, the accumulation rate of the radicals in the plasma-exposed polymer is written in Eq. (4).

$$\frac{d[P^*]}{dt} = k_1[P-H] - k_2[P^*]^2 \quad (4)$$

From Eq. (4), the rate of the hydroperoxide formation depends on  $\{k_1[P-H] - k_2[P^*]^2\}$ . When  $k_1[P-H] > k_2[P^*]^2$ , the hydroperoxide concentration will increase; when  $k_1[P-H] < k_2[P^*]^2$ , the hydroperoxide concentration will decrease; and when  $k_1[P-H] = k_2[P^*]^2$ , the hydroperoxide concentration will be constant. At an inflection point where the sign of  $\{k_1[P-H] - k_2[P^*]^2\}$  changes from plus to minus, a maximum of the hydroperoxide concentration appears. Thus, the profile of the hydroperoxide concentration in Figure 2 is not abnormal. The hydroperoxide concentration at the maximum in the Suzuki's experiment was  $2 \times 10^{15}$  numbers/cm<sup>2</sup>, which is higher by about 3 times than that in our experiment ( $6.0\text{--}6.3 \times 10^{14}$  numbers/cm<sup>2</sup>). This difference may be due to factors related to the plasma-operating conditions and the reaction system used for the plasma exposure.

### Graft Plasma Polymerization onto Kapton Film

Kapton films were exposed to an argon plasma operated at an RF power of 25 W to form hydroperoxides and reacted with vinylimidazole in a benzene solution at 70°C for 24 h. The graft polymerization of vinylimidazole was affirmed from the weight increase of the Kapton film. Figure 4 shows a typical result of the graft polymerization as a function of the argon plasma exposure time. The weight increase by the graft polymerization increases with increasing the argon plasma exposure, goes through a maximum, and levels off. The maximum weight increase appears at an argon plasma exposure time of 20 s and is about 0.9 wt % of the original Kapton film. Similarly, when the Kapton film was exposed to the argon plasma as a function of the RF power for 20 s, as shown in Figure 5, the weight increase by the graft polymerization increases with increasing the RF power, goes through a maximum at an RF power of about 25 W, and levels off at RF powers of more than 50 W. These two results indicate that the hydroperoxides generated in the Kapton film by the argon plasma exposure are able to initiate the graft polymerization of vinylimidazole, and that all the hydroperoxides generated in the Kapton film by the argon plasma exposure do not contribute to the initiation of the graft polymerization because the weight increase by the graft polymerization is not proportional to the hydroperoxide concentration. The argon plasma operation at an RF power as low

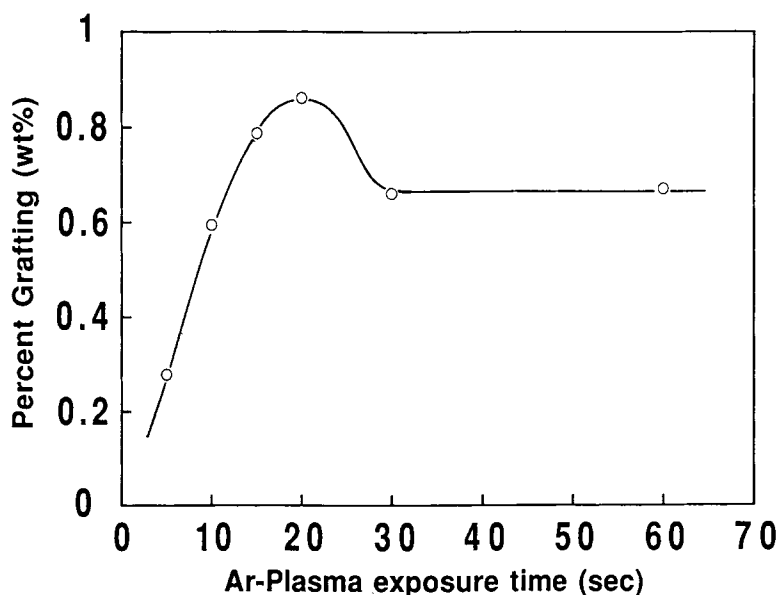
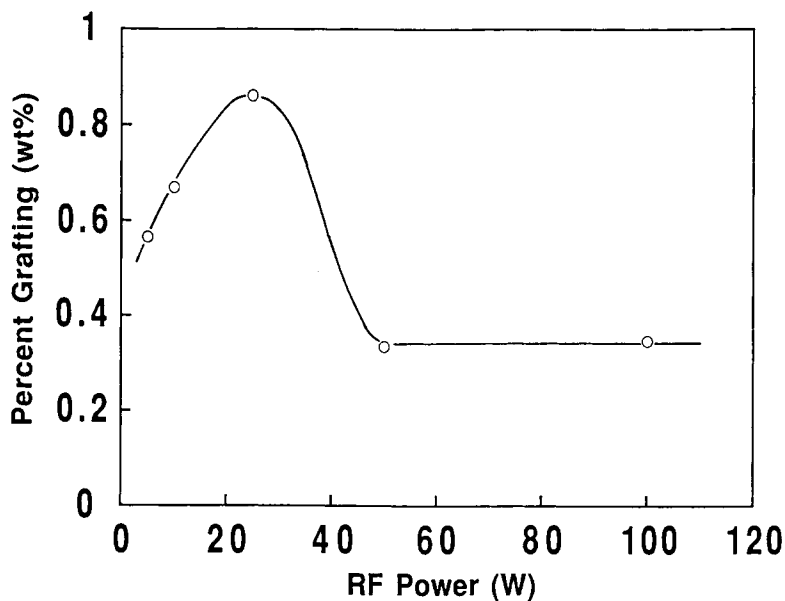


Figure 4 Percentage of graft polymers as a function of argon plasma exposure (RF power, 25 W).

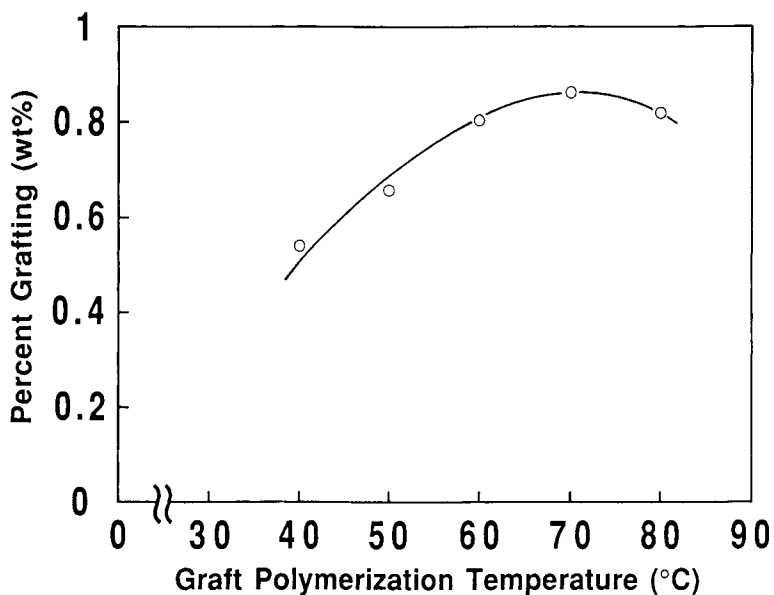


**Figure 5** Percentage of graft polymers as a function of RF power (argon plasma exposure time, 60 s).

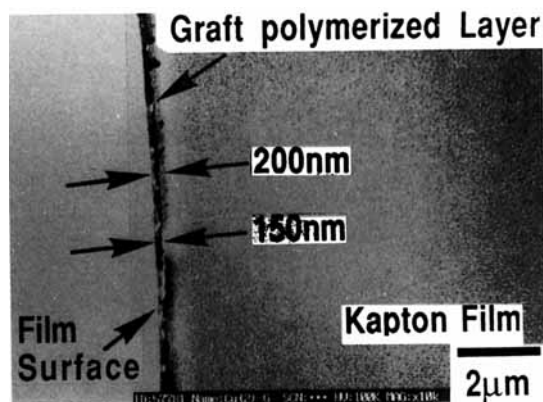
as 25 W and the plasma exposure time as short as 20 s are effective in the initiation of the graft polymerization. The temperature effect of the graft polymerization is shown in Figure 6 where the Kapton film was activated by the argon plasma exposure at an RF power of 25 W for 20 s and was graft-polymerized in a benzene solution of vinylimidazole (5 vol %) in temperature ranges of 40–80°C. Tem-

peratures around 70°C, as shown in Figure 6, is favorable to the graft polymerization.

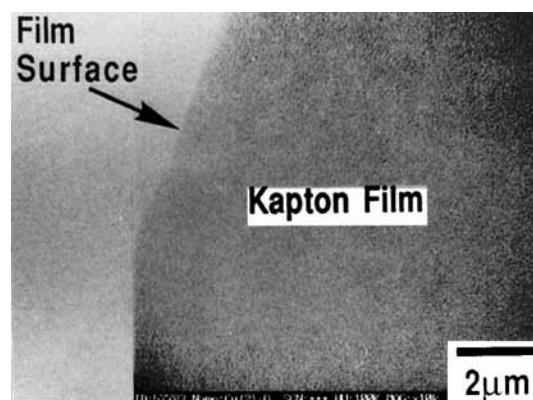
The vinylimidazole layer graft-polymerized onto the Kapton film was determined directly from the transmission electron microscope (TEM) picture of the cross section of the graft-polymerized Kapton film. Prior to the TEM observation, the vinylimidazole layer in the graft-polymerized Kapton film was



**Figure 6** Percentage of graft polymers as a function of polymerization temperature (RF power, 25 W; argon plasma exposure time, 60 s).



Plasma-graft-polymerized Kapton Film



Original Kapton Film

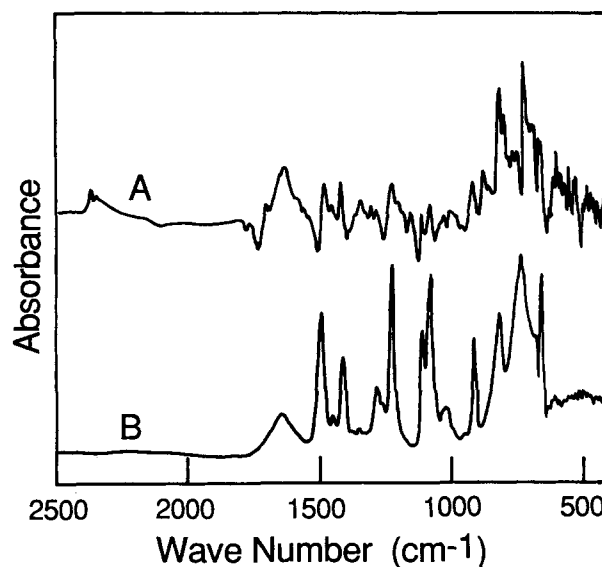
**Figure 7** TEM picture of cross section of vinylimidazole-graft-polymerized Kapton film and of original Kapton film.

dyed with copper ion. The dyed region (the graft polymer layer), as shown in Figure 7, is distinguished from the undyed region (Kapton film) by the light and shade of the TEM picture. The region dyed with copper ion (the graft polymer) is restricted at the Kapton surface and never inserts into the inside of the Kapton film, indicating that the graft polymerization occurred only at the outermost layer of the Kapton film. From the TEM picture, the vinylimidazole layer graft-polymerized is determined to be 150–200 nm thick, which corresponds to weight increases of 0.4–0.6 wt % under the assumption that the density of the vinylimidazole layer is unity. The weight increases estimated from the TEM picture (0.4–0.6 wt %) is nearly equal to the weight increase (0.9 wt %) determined directly from the weight measurement of the Kapton film before and after the graft polymerization.

ATR IR spectra of the graft-polymerized Kapton films were recorded. The difference in the IR spectrum between the graft-polymerized Kapton film and the non-graft-polymerized, but argon-plasma-treated, Kapton film was compared with the IR spectrum of polyvinylimidazole which was radically polymerized using dibenzoyl peroxide as an initiator. Polyvinylimidazole, as shown in spectrum B in Figure 8, shows characteristic, strong absorption peaks at  $1635\text{ cm}^{-1}$  (stretching vibration of  $\text{C}=\text{N}$ ),  $1495\text{ cm}^{-1}$  (stretching vibration of  $\text{C}=\text{C}$ ),  $1413\text{ cm}^{-1}$  (deformation vibration of  $\text{CH}_2$ ),  $1225\text{ cm}^{-1}$  (stretching vibration of  $\text{C}-\text{N}$  in imidazole ring),  $1108$  and  $1080\text{ cm}^{-1}$  (stretching vibration of  $\text{C}-\text{N}$ ); and  $914$ ,  $817$ ,  $738$ , and  $661\text{ cm}^{-1}$  (deformation vibration of  $\text{C}-\text{H}$ ).<sup>16</sup> The difference in the IR spectrum between the graft-polymerized Kapton film and the non-

graft-polymerized Kapton film, as shown in spectrum A in Figure 8, all characteristic absorption peaks due to polyvinylimidazole can be observed. There is no doubt from the difference in the IR spectrum that vinylimidazole was graft-polymerized at the surface of the Kapton film.

Conclusively, the TEM observation and the ATR IR spectrum show that vinylimidazole was graft-polymerized at the surface of the Kapton film by the plasma graft polymerization technique. The vinyl-



**Figure 8** ATR IR spectra of vinylimidazole-graft-polymerized Kapton film: (a) Difference IR spectrum between vinylimidazole-graft-polymerized Kapton film and argon-plasma-treated Kapton film, (b) polyvinylimidazole.



imidazole layer graft-polymerized at the Kapton film surface was 150–200 nm thick.

### Adhesion between Kapton Film Plasma-Graft-Polymerized with Vinylimidazole and Copper Metal

Effects of the surface modification by the graft polymerization of vinylimidazole on the adhesion between Kapton film and copper metal were investigated. For the investigation, the vinylimidazole-graft-polymerized Kapton film, the argon-plasma-treated but non-graft-polymerized Kapton film, and the original Kapton film were chosen as specimens. The vinylimidazole-graft-polymerized Kapton film was exposed to the argon plasma at an RF power of 25 W for 20 s and then was graft-polymerized with vinylimidazole at 70°C for 24 h. The argon-plasma-treated Kapton film was exposed to the argon plasma at an RF power of 25 W for 20 s. On each surface of their Kapton films, copper metal of 200 nm thickness was deposited by the vacuum evaporation technique, and then the surface of the copper metal was adhered with a sandblasted aluminum plate using an epoxide adhesive. Therefore, the adhesive joint used for the 180° peel strength measurement has a structure of the surface-modified or the original Kapton film–copper metal–epoxide adhesive–sandblasted aluminum plate. Table I shows the 180° peel strength of the three adhesive joints. The two surface-modified Kapton films, as shown in Table I, show improvement of the adhesion, especially the vinylimidazole-graft-polymerized Kapton film which shows 3.4 times higher in the 180° peel strength than that of the original Kapton film. Therefore, the surface modification by the graft polymerization of vinylimidazole is an effective way to improve adhesion between Kapton film and copper metal.

Scanning electron microscopy (SEM) pictures of the parts (Kapton film and copper metal sides) peeled-off from the adhesive joint show where the peeling-off occurred (Fig. 9). For the adhesive joint of the original Kapton film–copper metal, no copper metal, as shown in Figure 9(a), is observed at the

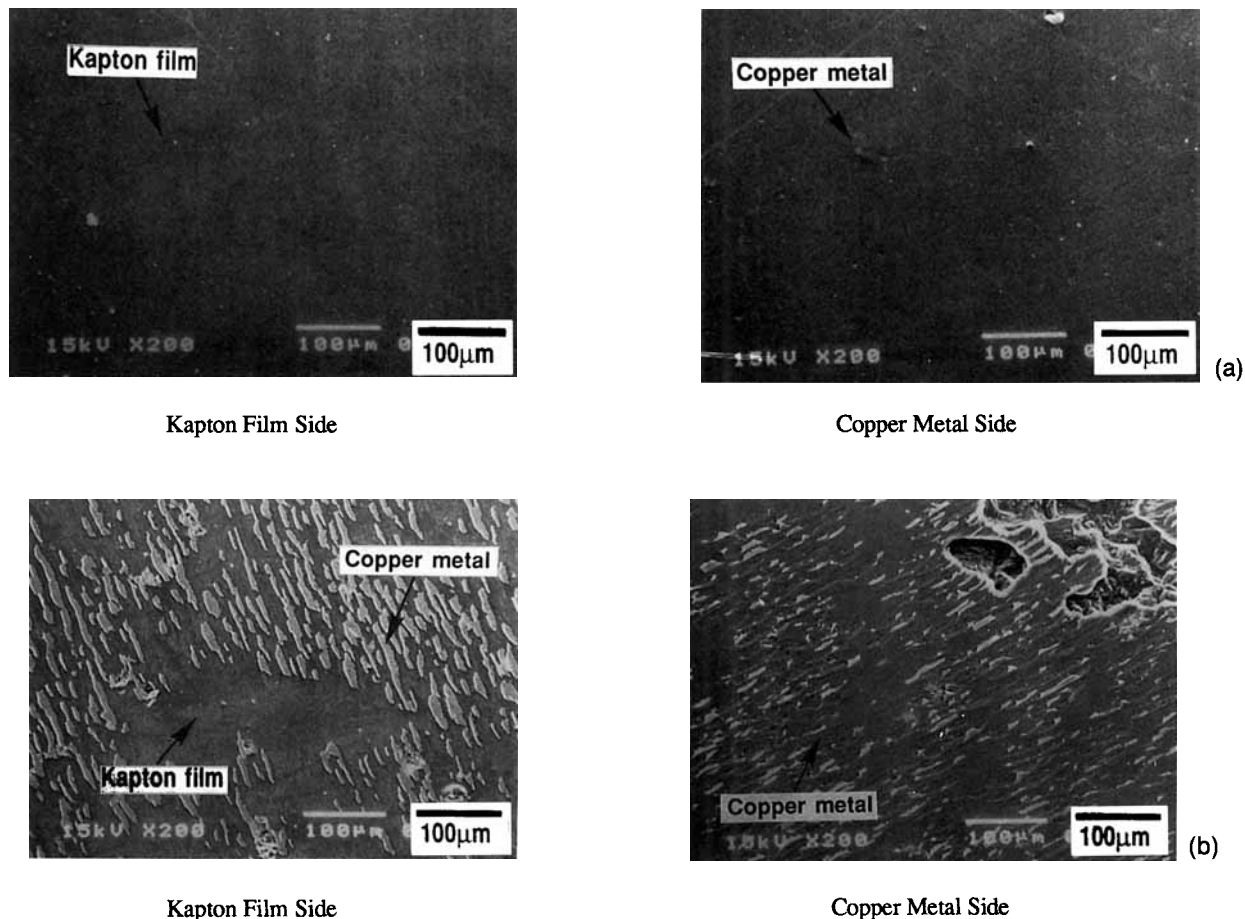
surface of the Kapton film side peeled-off, and no Kapton film is observed at the surface of the copper metal side peeled-off. This picture shows that the interaction between the original Kapton film and the copper metal is very poor, and that the failure occurred at the interface between the Kapton film and copper layer. While, for the adhesive joint of the vinylimidazole-graft-polymerized Kapton film–copper metal, copper metal in strips, as shown in Figure 9(b), is observed at the surface of the Kapton sides peeled-off from the adhesive joint. At the surface of the copper metal side peeled-off, Kapton film in strips is observed. These pictures show that the failure occurred at an inner part of the Kapton film or of the copper layer in some position and at the interface between the Kapton film and copper layer in the other position. Such a failure profile suggests that some chemical or physical interaction operated at the interface between the Kapton film and the copper metal. The chemical interaction means the formation of new chemical bonding between the grafted polyvinylimidazole and copper metal, and the physical interaction means the mechanical interlocking of the copper layer at the interface. Although these interactions cannot be evaluated separately from the peel strength measurement, the surface modification by the graft polymerization of vinylimidazole surely contributes to the improvement of the adhesion between Kapton film and copper metal.

### Interaction at Interface between Kapton Film and Copper Metal

The surface modification by the graft polymerization of vinylimidazole, as discussed in a previous section, contributes to the improvement of the adhesion between the Kapton film and copper metal. Whether some chemical interaction between the polyvinylimidazole graft-polymerized and copper metal operated or not was investigated by means of IR spectroscopy. On the vinylimidazole-graft-polymerized Kapton film, islands of copper metal at an average thickness of about 7.5 nm were deposited by the

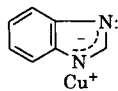
**Table I** 180° Peel Strength of Kapton–Copper Film Adhesive Joint

Adhesive Joint Structure	180° Peel Strength (N/5 mm)
Untreated Kapton film–copper film	0.41 ± 0.11
Argon-plasma-treated Kapton film–copper film	0.91 ± 0.12
Vinylimidazole-graft-polymerized Kapton film–copper film	1.40 ± 0.28



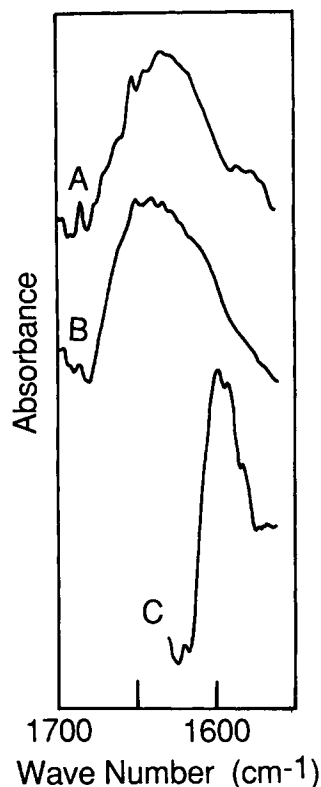
**Figure 9** (a) SEM pictures of parts (polymer side and copper side) peeled-off from adhesive joint of original Kapton film-copper metal. (b) SEM pictures of parts (polymer side and copper side) peeled-off from adhesive joint of vinylimidazole-graft-polymerized Kapton film/copper metal.

vacuum evaporation technique, and the IR spectrum of the copper-deposited films was compared with that of the non-copper-deposited Kapton film (Fig. 10). Xue et al.<sup>13</sup> reported that imino groups in benzimidazole interacted with copper metal at zero oxidation state to make a complex,



The formation of the complex was confirmed from the chemical shift of the XPS ( $N_{1s}$  and  $Cu_{2p}$  core level) spectrum. If imino groups in the vinylimidazole graft polymer made a complex with copper metal deposited on the graft-polymerized Kapton film, the position of the  $N=C$  stretching vibration would be shifted to lower wavenumber regions by the complex formation. The absorption peak due to the  $C=N$

stretching vibration for the vinylimidazole-graft-polymerized and copper-deposited Kapton film, as shown in Figure 10, becomes broader than that of the non-copper-deposited Kapton film, and a shoulder appears near  $1600\text{ cm}^{-1}$ . The difference IR spectrum between the copper-deposited Kapton film and the non-copper-deposited Kapton film shows obviously an absorption peak at  $1600\text{ cm}^{-1}$ . Therefore, it is not doubtful that a part of the deposited copper metal made a complex with imino groups in the vinylimidazole-graft-polymerized Kapton film. The complex formation surely increases the interaction between the Kapton film and copper metal and could contribute to the improvement of the adhesion between Kapton film and copper metal. However, this conclusion does not exclude the contribution of physical interactions (mechanical interlocking of copper layer).



**Figure 10** C=N stretching vibration shift by copper deposition on vinylimidazole-graft-polymerized Kapton film; (a) non-Cu-deposited Kapton film; (b) Cu-deposited Kapton film; (c) difference IR spectrum between spectrum B and A.

## CONCLUSION

Kapton film was modified by means of plasma graft polymerization for improvement of adhesion with copper metal. Vinylimidazole was graft-polymerized at the surface of the Kapton film. The graft-polymerized Kapton film showed good adhesion with copper metal. The interaction at the interface between the graft polymer and copper metal was investigated. The results are summarized as follows:

1. Argon plasma exposure generates hydroperoxides at the surface of Kapton film. The concentration of hydroperoxides generated by the argon plasma exposure depends on the RF power level and the plasma exposure time. An effective process is an exposure to the plasma operating at RF power as low as 20 W for exposure time as short as 60 s.
2. Hydroperoxides generated by the argon plasma exposure can initiate the graft polymerization of vinylimidazole. The graft poly-

mers are restricted at the surface of the Kapton film and never insert into the inside of the Kapton film. The graft-polymerized layer is 150–200 nm thick.

3. The surface modification by plasma graft polymerization of vinylimidazole led to the improvement of adhesion between Kapton film and copper metal. The 180° peel strength of the adhesion joint between the graft-polymerized Kapton film and copper metal was 3.4 times higher than that between the unmodified Kapton film and copper metal. A part of the copper metal makes a complex with the vinylimidazole chain graft-polymerized onto Kapton film. The complex contributes to the improvement of the adhesion.

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